On the Nature of Heat, as Directly Deducible from the Postulate of Carnot.

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1. The contemplation of the actual working of heat engines, and of their great development in England, with which he was well acquainted, suggested, to the mind of Sadi Carnot, the fundamental principle regulating their operation. He postulated that heat can give rise to mechanical work only in the process of carrying through its effort towards an equilibrium.* This idea involves immediately the whole of isothermal thermodynamics, including the modern thermodynamic potentials of physical chemistry; for it asserts that, in isothermal circumstances, the heat that is present takes no part in the interchanges of mechanically available energy in the material system, and therefore that the available energy is conserved by itself (or in part dissipated if the operation is irreversible) without any reference to the heat-changes which accompany its transformations.

An argument—perhaps the most original in physical science, whether as regards simple abstract power or in respect of grasp of essential practical principles—which was based on combining direct and reversed simplified engines operating in parallel, then led Carnot from this general postulate to a quantitative thermodynamic relation, fundamental for all departments of natural knowledge: that all reversible cyclic thermal operations, involving supply and abstraction of heat at the same two temperatures, have equal mechanical efficiency, which is the maximum possible. But he allowed himself, in his demonstration, somewhat reluctantly, and perhaps hastily in order to fix the ideas, to adopt the view then current that heat is substantial, so cannot be annulled or created. This point came right later, without trouble, in the corrected expositions by Clausius and W. Thomson, once a net of misconception, arising partly from confusion between total

* "La production d'une puissance motrice est donc due . . . . non à une consommation réelle de calorique, *mais à son transport d'un corps chaud à un corps froid*, c'est-à-dire à son rétablissement d'équilibre, équilibre supposé rompu par quelque cause que ce soit, par une action chimique, telle que la combustion, ou par toute autre . . . . D'après ce principe, il ne suffit pas, pour donner naissance à la puissance motrice, de produire de la chaleur : il faut encore se procurer du froid : sans lui la chaleur serait inutile . . . ." ('Réflexions,' ed. 1, p. 11 (1824); ed. 2, p. 6).

The unlocking of latent heat into sensible form could not be in itself on these principles a lapse towards equilibrium and so a source of motive power, because it is spontaneously reversible, there being no thermal effort in either direction.

energy and mechanically available energy, had been cleared away. The whole matter ought, however, to be capable of abstract development on broader and more general lines;* and the following statement is now advanced to that end. The rough manuscript notes left by Carnot at his death show his own early and very substantial progress towards a more complete doctrine of thermal motive power.

2. Suppose that motive power can be gained in a material system, by the carrying out of the effort of some entity, distributed through it, towards an equilibrium. Suppose that the state, as regards fall toward equilibrium, of this entity is determined in each element of mass of the system by only one variable, a potential belonging to it, so that when a path is open it will pass from an element of mass in which this potential is higher to one in which it is lower; also suppose that the effect is in simple proportion to the amount of the entity that enters into this operation, as the idea of a potential implies. Then it can be shown that only two possibilities are logically open. The entity may remain unchanged in amount, but may give rise to motive power in subsiding to a lower potential, just as a stream of water does in falling to a lower level, or a gas in expanding towards a uniform pressure. The other alternative is that, as regards giving rise to motive power by a reversible cyclic process, and therefore also generally, the scale of measurement of the entity may be so chosen that the entity will be used up to an amount equivalent to the motive power gained; and then, with suitable scale of measurement of the potential, the relation between them is defined by the statement that for all reversible paths between the same terminal configurations the amount of the entity that is added to the system at each potential divided by the potential at which it is added makes the same constant sum. Moreover, the first alternative arises in the analysis merely as the limiting form assumed by the second one, when the rate of exchange of the motive power in relation to the entity is indefinitely small.

But an exact general equation can subsist only for an interlacing plexus of possible operations which are not subject to wearing down or exhaustion: the freedom of the system must then be under adequate control, and the test is that its course is capable of reversal in all respects that are involved in doing work. The equation represents an optimum; when there is defect in

* In an interesting survey of thermodynamic history, Helmholtz expresses the contrary opinion: ". . . . what is still more noteworthy, it is hardly to be supposed that the principle in question could have been deduced from the more correct view, namely, that heat is motion, seeing that we are not yet in a position to establish that view on a completely scientific basis."—'Abhandl.,' iii, p. 594, in a review of Lord Kelvin's 'Papers,' from 'Nature,' 1885.

the control, so that the system can slip away, the quantity otherwise always constant must increase.

Thus, on the basic Carnot idea that motive power arises only from the carrying through of the effort of heat towards equilibrium, and that some of the possible power is dissipated when the operations are not reversible, it follows that there can be *a priori*, only two possible modes of action :

(1) The heat may fall to lower potential unchanged in amount, as in the cases of water-power, gravitational or electric attraction, etc.

(2) The heat may be itself consumed in part; in which case the heat can be measured on such a calorimetric scale that there is equivalence between the motive power that is gained and the heat that is lost. This alternative proves to be the actual one for heat; which thus ranks, as regards quantity, but not as regards complete freedom of exchange, with the other forms of natural energies, and is not of the nature of a substance.

There is no third choice open: assuming, of course, that the field of operation partakes of the general characteristic of the order of nature, in that it is rationally explicable, and does not present arbitrary uncorrelated discontinuities.

The fundamental idea of Carnot, in its original form and the most natural one, as above stated in 1824, nearly a century ago, thus involves, in itself alone, either that heat is a substance, or that heat, under the circumstances when it is converted into mechanical energy, always passes in equivalent amount.

3. The argument on which these conclusions can be maintained proceeds as follows, any implication as to the nature of heat being at this stage necessarily avoided. If a reversible cyclic engine, exchanging heat with outside bodies at only two temperatures θ_1 and θ_2, were less efficient than some other type of engine, also taking in heat (H_1) at only one temperature θ_1 and giving out heat (H_2) at another θ_2, then the reversible engine, using the work done by this latter engine to operate it in the reverse direction, would restore heat more than H_1 to the source. If, therefore, the reversed engine is operated so as to restore only the same amount of heat H_1 to the source, then in the working of the compound engine constituted of the direct and reversed ones thus coupled in parallel, work will, on the whole, be done; while there would be no abstraction of heat from outside bodies at the higher of the two temperatures, and therefore no fall of heat towards equilibrium of temperature; and this contradicts Carnot's postulate. The work produced would, in fact, have to be done through the mere vanishing of some heat at the lower temperature, if there is any heat-change at all, for no other cause would be assignable; and this process could go on without end. Thus the

negation of the proposition that the efficiency, defined by work done W_{12} divided by heat H_1 received at the higher temperature, is the maximum possible for a reversible engine, as compared with any other engine working between the same two temperatures of supply and rejection of heat, leads to a result deemed to be impossible. When this is granted, it follows, after the manner of Carnot, that all such simple reversible engines have the same efficiency, which is a function of the two temperatures θ_1 and θ_2 alone. This demonstration seems to be free from any assumption as to the nature of heat.

4. Stated in terms of the simplified reversible thermal engine—introduced by Carnot to render the subject amenable to exact reasoning—which takes into its working system heat H_1 at temperature θ_1 alone and rejects H_2 at θ_2 alone, thereby doing work W_{12} available for external use in a cyclic manner, the extended mode of argument, on which the further conclusions stated above are based, may be set out briefly as follows. As just shown, for any such reversible engine,

$$W_{12}/H_1 = F(\theta_1, \theta_2).$$

Also, the same formula must apply to the working of the same engine reversed, for there would otherwise be breach in physical continuity; thus

$$W_{21}/H_2 = F(\theta_2, \theta_1)$$

where

$$W_{12} = -W_{21}.$$

Let now, following Carnot, the step of temperature $\theta_1 - \theta_2$ be infinitesimal, say $\delta\theta$. Then we might proceed *tentatively* (in order to exhibit the necessary precautions) to reason as follows:

$$\frac{W_{12}}{H_1} = F(\theta_1, \theta_1) + \frac{\partial F(\theta_1, \theta_1)}{\partial \theta_1}(-\delta\theta)$$

$$\frac{W_{21}}{H_2} = F(\theta_2, \theta_2) + \frac{\partial F(\theta_2, \theta_2)}{\partial \theta_2}\delta\theta$$

where in $\frac{\partial F(\theta, \theta)}{\partial \theta}$ the differentiation applies only to the second θ in the functional bracket. If we represent the function thus denoted by the reciprocal of $-f(\theta)$, we have, since $F(\theta, \theta)$ must itself vanish,

$$W_{12} = \frac{H_1}{f(\theta_1)}\delta\theta = \frac{H_2}{f(\theta)_2}\delta\theta.$$

Thus

$$\frac{H_1}{f(\theta_1)} = \frac{H_2}{f(\theta_2)} = \frac{W_{12}}{\delta\theta}$$

giving for the infinitesimal range with which we are now concerned

$$H_1 - H_2 = W_{12}\frac{f(\theta_1) - f(\theta_2)}{\theta_1 - \theta_2}.$$

If, then, a new scale of temperature Θ is adopted, such that $\partial f(\Theta)/\partial\Theta$ is unity *i.e.*, if $f(\theta)$ is replaced by Θ, which is W. Thomson's absolute scale, we have

$$\frac{H_1}{\Theta_1}=\frac{H_2}{\Theta_2} \qquad \text{and} \qquad H_1-H_2 = W_{12};$$

the only alternative being an exceptional or rather limiting case for which $f(\theta)$ is constant, say, B^{-1}, and then $H_1 = H_2$, while $W = BH(\theta_1-\theta_2)$.

The argument could now be extended to a finite range of temperature, in Carnot's manner, by coupling engines of infinitesimal range in series, so that the heat from each feeds the next.

5. Further scrutiny of this mode of reasoning by way of Carnot's function of a single variable is, however, demanded: for at first sight it would seem to be equally open to us to infer, for the infinitesimal range under consideration,

$$\frac{W_{12}}{H_1}=\frac{\delta\theta}{f(\theta_2)}, \qquad \frac{W_{21}}{H_2}=\frac{-\delta\theta}{f(\theta_1)}$$

giving

$$\frac{H_1}{f(\theta_2)}=\frac{H_2}{f(\theta_1)}=\frac{W_{12}}{\delta\theta}$$

and so

$$H_1-H_2 = -W_{12}\frac{d}{d\theta}f(\theta).$$

Thus, if we choose the scale of θ so as to ensure equivalence of heat and work $W_{12} = H_1-H_2$, then $-f(\theta)$ becomes Θ and therefore $H_2\Theta_2 = H_1\Theta_1$, differing from the previous result.

But this procedure is ruled out: for the same formula must hold also for infinitesimal ranges shorter than $\theta_1-\theta_2$, starting with θ_1, which shows that the ratio of the work to the heat-supply H_1 must be put equal to a function of the temperature θ_1 of that supply, multiplied by the variable infinitesimal range.

6. Indeed, on such an order of ideas as we have just now rejected, this ratio of work to heat ought to be the Carnot function of the mean of the temperatures multiplied by the range; but that would be too narrow a view, as it would necessitate equality of H_1 and H_2, and therefore a substantial nature for heat. In the earlier papers of W. Thomson, he, in fact, does compute the value of Carnot's function at the temperature $\frac{1}{2}°$ C. in order to apply it to a range of working from 0° C. to 1° C.; thus here we have probably a main cause of that perplexity which led him even to ignore, provisionally, for a year or two, Joule's principle, in order, as he thought, to save that of Carnot. Clausius was more fortunate: his analysis, after Clapeyron, measuring temperature from the first by the expansion of a perfect gas, assumed to

have no internal potential energy, and working concretely with the simple gas cycle, went straight to its goal, and did not encounter at all this arresting type of paradox.

7. But even our previous deduction for an infinitesimal range of working requires much further support. For the purpose to which it is applied, the expansion of $F(\theta_1, \theta_1 - \delta\theta)$ ought to proceed up to the term involving $\delta\theta^2$; and then, as it stands, the conclusion could not be drawn.

A point of exposition and demonstration, cognate to the present one, arises in a closely related case, that of Hamilton's general dynamical equation of variation of the action, which is sometimes also in this regard faultily developed. There also, it is an affair of passing from one state of motion, between assigned terminal configurations, to another that is variationally near it. In passing from an actual motion to an adjacent motion, frictionlessly constrained in any manner and so possessing constant energy, and having the same terminal configurations, but without further restriction, the variation of the action, expressed by $\delta\int 2T dt$, always vanishes; so that, provided the path of the dynamical system does not pass beyond the next kinetic focus, the action is minimum. But notwithstanding, an analytical equation of variation of the action, in terms of the variations of the terminal configurations alone, and of the energy of the system, subsists only when it is *actual free paths* that are compared. Otherwise, *second* differentials of the action, derived from this variational expression regarded as implying that it is a function of initial and final configurations and energy alone, could have no definite values, in fact could not exist. The necessity of this distinction, always obvious in special applications of variation of the action, such (*e.g.*, Hamilton's own optical rays) as usually form the guide to wider generalisations, is laid down explicity in the general statement in Thomson and Tait's 'Nat. Phil.,' § 329: Jacobi employs a more algebraic order of ideas in which it is latent.

The thermal procedure above, involving adjacent direct and reversed paths differing by reason of an infinitesimal change of temperature, might be reconstituted on a sound basis after this model. But it is clearer to construct an argument once for all in terms of finite ranges of temperature.

8. If in the operation of a Carnot reversible engine, absorption from outside of heat H_1 at temperature θ_1 and rejection to outside of H_2 at θ_2 leads to the production of motive power W_{12} which can be transmitted mechanically to external uses, then by the argument developed above

$$W_{12}/H_1 = F(\theta_1, \theta_2): \text{ where } F(\theta_1, \theta_1) = 0.$$

If we may postulate as before that this formula must rest on a rational

physical basis, then it must apply also to the reversed working of the engine*: thus

$$-W_{12}/H_2 = F(\theta_2, \theta_1).$$

Therefore
$$\frac{H_1}{H_2} = -\frac{F(\theta_2, \theta_1)}{F(\theta_1, \theta_2)} = f(\theta_1, \theta_2),$$

here introducing an abbreviated functional symbol $f(\theta_1, \theta_2)$.

But two such engines $\{H_1, H_2\}$ and $\{H_2, H_3\}$ can be coupled to work in series, so that the heat H_2 rejected from the first at θ_2 feeds the second at the same temperature. For this compound reversible engine the formula gives

$$\frac{H_1}{H_3} = -\frac{F(\theta_3, \theta_1)}{F(\theta_1, \theta_3)} = f(\theta_1, \theta_3).$$

Thus we have the functional relation

$$f(\theta_1, \theta_3) = f(\theta_1, \theta_2) f(\theta_2, \theta_3).$$

This expression on the right for $f(\theta_1, \theta_3)$ involves an arbitrary parameter θ_2: moreover, it exhibits that function as the product of a function of θ_1 and a function of θ_3. These features can arise only through a relation of the form

$$f(\theta_1, \theta_2) = g(\theta_1)/g(\theta_2).$$

Thus
$$H_1/g(\theta_1) = H_2/g(\theta_2) = H_3/g(\theta_3), = k \text{ say.}$$

Moreover
$$W_{12} + W_{23} = W_{13}$$

where
$$W_{12} = kg(\theta_1) F(\theta_1, \theta_2) = k\phi(\theta_1, \theta_2) \text{ say}:$$

so that we have
$$\phi(\theta_1, \theta_3) = \phi(\theta_1, \theta_2) + \phi(\theta_2, \theta_3)$$

whatever be the value of θ_2: which requires that

$$\phi(\theta_1, \theta_2) = \psi(\theta_1) - \psi(\theta_2).$$

Thus
$$W_{12} = k\phi(\theta_1, \theta_2) = H_1 \frac{\psi(\theta_1) - \psi(\theta_2)}{g(\theta_1)}.$$

Therefore finally
$$\frac{H_1}{g(\theta_1)} = \frac{H_2}{g(\theta_2)} = \frac{W_{12}}{\psi(\theta_1) - \psi(\theta_2)};$$

so that
$$W_{12} = H_1 \frac{\psi(\theta_1)}{g(\theta_1)} - H_2 \frac{\psi(\theta_2)}{g(\theta_2)}.$$

9. The scales of measurement of heat and temperature are in these abstract formulæ as yet entirely unspecified. If we now fix the measurement of quantities of heat in terms of a new ideal standard calorimetric substance, whose law of specific heat differs from that of the previous one by the

* This can, however, be made a matter of deduction: for if a different function of θ_2, θ_1, is assumed to apply to the thermal motor used reversed as a pump for raising heat to higher level of temperature, the same type of argument as in this paragraph will lead to the same final results.

multiplier $\psi(\theta)/g(\theta)$, the ratio of work gained to heat lost in a cycle of finite range will become unity, $\psi(\theta)$ replacing $g(\theta)$ in the final formulæ. This choice of calorimetric substance will therefore establish quantitative equivalence between work gained and heat lost: and there is no reason why this result should remain restricted to reversible processes. Finally, we are obviously invited to select the one remaining function $\psi(\theta)$ as the normal measure of the standard temperature Θ; so that now for any finite range of temperature the formulæ for a Carnot engine become

$$\frac{H_1}{\Theta_1} = \frac{H_2}{\Theta_2} = \frac{W_{12}}{\Theta_1 - \Theta_2}.$$

The one exception to this deduction is its own limiting case, that $g(\theta)$ may be a constant, say B^{-1}. Thus $H_1 = H_2$ and $W_{12} = BH\{\psi(\theta_1) - \psi(\theta_2)\}$; so that we would still be invited to select $\psi(\theta)$ as absolute temperature, and the motive power would arise from the fall of the heat, unchanged in amount, through the range of temperature, exactly after the analogy of the fall of a stream of water through a change of level.

10. The whole formal theory of heat engines, and of thermodynamic processes in general, is thus developable in a purely abstract manner from Carnot's own initial idea, that heat can give rise to motive power only in the process of carrying through its effort towards equilibrium. Starting from this postulate, it is left to experience merely to decide between two sharply contrasted alternatives, whether (1) heat is virtually a substance doing work merely by falling to a lower level of temperature, or, on the other hand, (2) it is a form of energy, presumably of a fortuitous molecular type, which can be rearranged in part into ordered or mechanical energy by taking advantage of its innate effort to run down towards a dead level of distribution.

The kinetic energies of the molecules in a small element of mass will, in fact, mix together far more rapidly towards an equilibrium of distribution in that element than will the energies distributed through a large volume of the substance; thus in the static type of theory to which thermodynamics is restricted, each element of mass is assumed to have already a temperature. But the energy existing at this dead level of temperature in the infinitesimal elements can be in part recovered or reconstituted into energy arranged in finite groupings in these elements, thus becoming partly regularised and therefore of mechanical type, when suitable advantage is taken of the further effort towards equalisation of temperature between the elements and throughout the whole mass.

11. It still remains, on this order of ideas, to identify physically the scale

of temperature for which the formulæ become simplified as above, and also to ascertain that the usual calorimetric substances do not differ very substantially, within the usual ranges of temperature, from the ideal one which allows heat to be thus measured as energy.

In the ideal perfect gas of Joule and Waterston and Clausius, the molecules exert mutual forces only in the instant of encounter, their range being thus so short that only negligible mechanical work is thereby involved: there is no internal potential energy, and all the energy that such a substance receives passes into the form of kinetic energy of the un-coördinated motions of the molecules, which may be named internal heat. The pressure is, as Joule proved, equal to $\frac{2}{3}\tau'$, where τ' is the translatory part of the molecular energy per unit volume: this is $\frac{2}{3}k\tau$, where τ is the whole of that energy and k must be constant. Therefore, the heat received by a mass of such substance finds a measure in the change of volume produced by it under constant pressure; so that if also temperature is measured by its expansion, this will be the standard calorimetric substance. But what is the relation of temperature thus measured to the ideal absolute temperature? The working cycle for a gas, expounded and scrutinised* in the necessary close detail by Carnot as a typical precise example of his conception of a reversible cyclic process, shows that the two are identical. Thus a gas satisfying approximately the ideal gaseous laws realises, practically, as Clausius was the first formally to disentangle, the normal scales of temperature and of calorimetry, which Carnot's idea by itself had already implicitly contained.

The experimental checking of the results, to an extent adequate to ensure confidence, is, of course, a necessary supplement to any abstract argument concerning natural processes; and after that there still remains the concrete

* The development of heat in the gas by compression he has to accept as a fact on the basis of the familiar experiments and of Laplace's correction to the velocity of sound-waves; for by adopting the current view he has debarred himself from the idea of creation of new heat from work. In the algebraic analysis for gas-cycles (ed. 2, footnote, p. 40), he is thus led to results confused and in part suspect, and consequent recurring remarks (*cf.* p. 50) on the doubtfulness of the current theory of heat, which he had adopted. He is thus puzzled by the result of expansion of the gas into a vacuum reservoir, as found by Guy Lussac and Welter, the one vessel gaining as much heat as the other loses; but later, in his posthumous notes (p. 91), he attains to nearly complete illumination. Thus in the same context ('Notes inédites,' p. 96), we even find a suggestion of the Joule-Thomson experimental method: "Faire sortir de l'air d'un vaste réservoir où il est comprimé, *et rompre la vitesse* dans un large tuyau où se trouvent placés des corps solides, mesurer la température lorsqu'elle est devenue uniforme. Voir si elle est la même que dans le réservoir. Mêmes expériences avec d'autres gaz et avec la vapeur formée sous diverses pressions . . . ." He points in passing to reduction of temperature with height in the atmosphere as due to the convective equilibrium investigated later by W. Thomson (ed. 2, footnote, p. 16).

dynamical realisation or reconstitution of the subject, so far as possible, in terms of the molecular constitution of matter.

12. If then Carnot's original idea is well founded, that heat can give rise to work only in carrying through its innate effort towards an equilibrium, as water does in its effort towards a lower level, or a gas in its effort to expand towards a uniform pressure, it follows necessarily that heat is measurable as regards quantity in the same terms as motive power. The physical alternative, that heat may be virtually a substance, appears in the abstract argument merely as a limiting case, when the ratio of equivalence is indefinitely small and the amount of heat therefore does not sensibly vary.

But although the preliminary idea of Carnot, apart from the semi-practical development that accrued to it in his further logical analysis of heat-engines and other thermal processes, was almost co-extensive with the modern doctrine of chemical dynamics, yet in 1824, nearly a century ago, the scientific material did not exist for any systematic search into the ramifications of such a principle of available isothermal energy throughout nature. Carnot was duly impressed with the fact that chemical combination in the furnace is an essential part* of the phenomenon which he explores and analyses; but he had to take up the position that for the purposes of his discussion it enters only in a preliminary way, as the means of providing the heat with which the engine works; and elsewhere he notes the production of motive power by electric means as beyond the range of his argument.

The principle of available isothermal energy in nature is in fact far wider than its thermal province, though the latter is an inseparable part of it. Its development must depend on a reasoned survey of the operations of nature in their wider aspects. Thus it is not so surprising that the principle of Joule should have been recognised in its full scope, as an exact law, only twenty years later. But we find the preliminary notion of conservation and interchange of natural energies already confidently and acutely expanded by Faraday, to whose manifold discoveries in the correlation of the physical agencies it seems, in his own vivid but undefined intuition, to have formed a main guide. No instance of this is historically more instructive than the remonstrance in one of his later researches against the partial interpretation of Volta's original investigations, that the phenomena of the voltaic pile can be founded solely on electric forces of mere contact between different substances. Thus†

"2071. The contact theory assumes in fact . . . that—without any change in the acting matter or the consumption of any generating force—a current

* He recognises that the essential datum is the maximum temperature at which the combustion can be sustained.

† 'Exp. Res.,' xvii, January, 1840.

can be produced which shall go on for ever against a constant resistance, or only be stopped as in the voltaic trough by the ruins which its exertion has heaped up in its own course. This would indeed be a creation of power and is like no other force in nature. We have many processes by which the form of the power may be so changed that an apparent *conversion* of one into another takes place. So we can change chemical force into the electric current, or the current into chemical force. The beautiful experiments of Seebeck and Peltier show the convertibility of heat and electricity; and others by Oersted and myself show the convertibility of electricity and magnetism. But in no case, not even those of the Gymnotus and Torpedo (1790) is there a pure creation of force: a production of power without a corresponding exhaustion of something to supply it."

"2073. Were it otherwise than it is, and were the contact theory true, then it appears to me, the equality of cause and effect would be denied (2069). Then would the perpetual motion idea be true: and it would not be at all difficult, upon the first given case of an electric current by contact alone, to produce an electro-magnetic arrangement which, as to its principle, would go on producing mechanical effects for ever."

In a footnote he quotes from Roget (1827) to the effect that physical effort of any kind appears to be unable to carry itself through without drawing upon and partially exhausting its limited reserves: and he might have quoted a footnote of Carnot (*infra*), introducing this very subject of the voltaic pile, had it been known to him.

13. In this special controversy about contact forces, which has persisted down to our own time, a sharp discrimination between two distinct ideas, force and energy, is what had been mainly lacking. In the eighteenth century a cognate controversy as to whether force should be measured by the *momentum* or by the *vis viva* produced by it, long raged: the final stage in appeasing it was the introduction of the necessary new term *energy* by Young* to represent the accumulated *vis viva* of a force, which Leibniz and his school, and many others including the engineer Smeaton, had insisted on taking as its measure, instead of the Newtonian *momentum*. The expansion, rather than correction, of ideas that was thus involved—the distinction between force and energy, between effort and its consummation—may be compared with another classical instance of clarification, W. Thomson's recognition of available energy as distinct from total energy, of which the germ was latent, for development in the fullness of time, in Carnot's term motive power.

Two years after these remarks of Faraday, the idea of energy as conserved and interchangeable in natural processes was grasped firmly and developed

* 'Lectures,' vol. i, p. 78 (1807).

in many subtle aspects by the physiologist J. R. Mayer: while Joule was already engaged in the experiments that confirmed his own precise and practical outlook, and constituted it the fundamental generalisation of physical science. Finally, the doctrine was crystallised by Helmholtz in his famous essay of 1847, building on the ideas and experiments of Joule, as a quantitative guide through the correlations of natural agencies,—stimulated thereto in the main, as was also Young, by study of the mathematical physicists of the previous century, and indeed without much immediate local recognition except from the mathematician Jacobi. But even this formulation of the conservation and interchange of potential motive power in nature is incomplete until the condition implied in Carnot's fundamental idea is added to it, that the operations must take place at uniform temperature, or else be subject to the other limitations of thermodynamics.

But the ideas of Carnot on this subject are as definite as those of Helmholtz or of Thomson. On the theoretical abstract side nothing has been added, except by way of further exemplification, to his reasoned footnote on the principle of the *perpetual motion.** The principle has, he states, been demonstrated only for mechanical actions: "Mais peut-on concevoir les phénomènes de la chaleur et de l'électricité commes dues à autre chose qu'à des mouvements quelconques de corps, et commes tels ne doivent-ils pas être soumis aux lois générales de la mécanique?" And he goes on to assert, as an example, the inevitable exhaustion of the power of the pile of Volta, owing to the work that it performs. In the text to which this footnote refers the implication is that heat as well as electricity is a substance, and that the phenomena arise from its disturbance. Thus ". . . tout rétablissement d'équilibre [dans le calorique] qui se fera sans production de cette [maximum] puissance devra être considéré comme une véritable perte; . . ." The principle of the thermal dissipation of available energies, in extension of the simpler principle of the complete availability of isothermal energies, is here almost in sight. His thoughts recur to the latter subject, now however on a definite mechanical theory of the nature of heat, but still in a tentative way, in the posthumous fragments (p. 92) published in 1878 by his brother.

The master thought which presides over all this development of physical science was enunciated by Sadi Carnot in 1824, in a solitary essay nearly contemporary with the chief work of his great countrymen Ampère and Fresnel. As a chapter in scientific method, it seems desirable even now to bring the full individual potentiality of this creative idea into view.

* 'Réflexions,' ed. 1, p. 20; ed. 2, p. 12.

[*Added February* 26.—The main thesis developed above is that a close analysis of the postulate of Carnot evolves from it not one but two equations. These may be interpreted, after suitable simplification of scales of measurement of heat and temperature, as asserting that when there is no waste of power, two quantities are conserved, viz., heat *plus* other forms of energy, and entropy: when however irreversible features are present, the latter must increase while the constancy of the former need not be disturbed. Yet, as Helmholtz remarked, the distinction between the two constituents of this constant sum, the heat in a body and its other forms of internal energy, has hardly even now become analytically precise.

My attention has now been recalled by Sir Alfred Ewing to a very interesting and in certain respects cognate discussion by Prof. H. L. Callendar,* which turns on the idea that the caloric, whose conservation had been *assumed* by Carnot, is capable of being interpreted as entropy, so far as reversible processes are concerned. He there recognises, as above, that the efficiency principle can be established without any assumption as to the nature of heat. Then the basic postulate would take the form that motive power can be gained only in carrying through the effort of this caloric towards its equilibrium distribution, and would arise from part of the energy, of its disturbance from equilibrium, being diverted into mechanical work. The motive power thus gained would be equal to the caloric that is transferred, multiplied by its fall in potential as measured by the temperature associated with it: but there would be no necessary absolute zero. The entity heat would, on this train of ideas, enter as mere residual energy, of amount required to satisfy Joule's experimental law of conservation. But wherever the energy of disturbance of the caloric is transformed in a wasteful (because irreversible) manner, there would have to be creation of new caloric, of amount equal to work wasted, divided by temperature, thus implying an absolute zero; it would be imaginable, perhaps, as a sort of degenerate residue from lost motive power. The reversible disappearance of free electricity, or even free heat, by becoming latent, is hardly an analogy in point.

This great fluidity of ideas as to specification of heat, or rather of caloric, has its source in the necessity of postulating a provisional calorimetric substance, after the manner of Black, the unit of heat being proportional to its thermal capacity which may be any function of temperature: thus heat will be an equivalent of vanished energy only when it is measured on the proper scale; while even entropy would assume the *rôle* of caloric provided the thermal capacity of the calorimeter were taken proportional to absolute temperature.

* Presidential Address to the Physical Society, February 10, 1911.

Reference may also here be made to Clausius' long-sustained attempt (which received some favour from Willard Gibbs in his Obituary Notice of Clausius, *Collected Papers*, ii, p. 263) to break up the Carnot cycle into two physically distinct parts, the direct transformation of heat Q′ into work at temperature θ', and a compensating transference of heat Q from temperature θ_1 to a lower temperature θ_2.]

The Absorption of the Radiation emitted by a Palladium Anticathode in Rhodium, Palladium and Silver.

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[PLATE 3.]

Introduction.

The analysis of a beam of rays from an X-ray bulb by reflection at a crystal face shows that the bulb emits a continuous spectrum of radiation upon which are superposed a few wave-lengths which stand out prominently from the rest, these being the characteristic wave-lengths of the metal of the anticathode. Much note has not been taken hitherto of the general radiation, more attention having been paid to that part of the spectrum in the immediate vicinity of the characteristic rays. In the present work an attempt is made to obtain fuller knowledge of the general radiation by studying the absorption coefficients of the rays in the three elements rhodium, palladium, and silver. In the particular bulb chosen, palladium is used as the metal of the anticathode.

Apparatus.

The apparatus used in the investigation is the Bragg X-ray spectrometer, a full description of which may be found in Bragg's book on "X-ray and Crystal Structure," p. 22 *et seq.* A beam of rays, leaving the anticathode at a grazing angle, passes through two slits before falling on the crystal. The slit nearer to the crystal is movable and can be brought up very close to the crystal. After reflection, the beam passes through a third slit on its way to the ionisation chamber. We shall allude to these three slits as the bulb slit, crystal slit, and chamber slit respectively.

It is essential in an investigation of this nature to use a crystal which gives